The theory of resonance in chemistry

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The theory of resonance in inorganic and organic chemistry was largely formulated in the period 1927 to 1933 on the basis of the quantum-mechanical theory of the singlet and triplet states of the helium atom that was developed by Heisenberg in 1926 and was given the name quantum-mechanical resonance by him. Some incorrect and seriously misleading remarks about the theory and my part in its development are made in the recently published (1976) Biographical Memoir of Sir Robert Robinson, who in 1926 had made an important contribution to the formulation of the pre-quantum-mechanical electronic theory of the structure and properties of organic molecules. It is pointed out that these remarks have little basis in fact and are based almost entirely on misunderstanding or incompleteness of knowledge of the nature and early history of the theory of resonance.

1. INTRODUCTION

The concept of quantum-mechanical resonance was developed by Heisenberg (1926) in connection with the discussion of the singlet and triplet quantum states of the helium atom. The concept is based on the principle that the correct wave function for a state of a system (such as the normal state) can be expressed as a sum of functions constituting a complete set. The concept was then applied by Heitler & London (1927) to the normal state of the hydrogen molecule. They formulated a wave function corresponding to placing the electron with positive spin in a 1s atomic orbital about the first nucleus and the electron with negative spin in a similar orbital about the second nucleus, and another function in which the two electrons were interchanged. The calculated energy for either one of these functions alone was found not to correspond to the formation of a stable bond between the two atoms, whereas that for the sum of the two functions did correspond to formation of a bond with bond energy nearly as great as that observed. The molecule was described as involving the resonance (exchange) of the electrons between the positions about the two nuclei, and the bond energy was attributed largely to the resonance energy (exchange integral). A similar treatment, involving resonance of one electron between the 1s orbitals about the two nuclei, was developed for the hydrogen molecule ion (Pauling 1928a). The theory of resonance was then used (Pauling 1928b) to explain the observed equivalence of the four bonds formed by the carbon atom, thus resolving the problem posed by the non-

equivalence of the 2s orbital and the three 2p orbitals. This was the start of the theory of hybrid bond orbitals, which was then developed further (Slater 1931a; Pauling 1931a). The theory led to the discovery of the three-electron bond (Pauling 1931b), the partial ionic character of covalent bonds (Pauling 1929, 1932a) and the resonance of molecules between two or more valence-bond structures (Hückel 1931; Slater 1931a; Pauling 1932b). After Slater (1931b) had formulated the wave functions for valence-bond structures of molecules and evaluated the corresponding matrix elements and I (1933) had discovered a simple graphical method of determining their coefficients, extensive valence-bond calculations were made for aromatic and conjugated hydrocarbons and other substances (Pauling & Wheland 1933; Pauling & Sherman 1933; also others). These calculations, as well as calculations made by the molecular-orbital method and extensive experimental studies of bond lengths and other properties, provided the basis for the significant refinement and increase in power of the chemical structure theory of both inorganic and organic substances. The quantum-mechanical basis of the theory was discussed in detail by Pauling & Wilson (1935). The theory of resonance is now treated in essentially every textbook of chemistry and is used by essentially every chemist.

The usefulness of the theory of resonance may be illustrated by mention of the part it played in the discovery of the alpha helix and the parallel-chain and anti-parallel-chain pleated sheets, the most important secondary structures of poly-peptide chains in proteins (Pauling & Corey 1950, 1951). In one of my first papers on the theory of resonance (1932b) I had used the amide group (peptide group) as an example, and had pointed out that the bond between the carbonyl carbon atom and the nitrogen atom has a considerable amount, later estimated as 40 %, of double-bond character, which requires that the six atoms adjacent to this bond be coplanar. It was this knowledge that permitted the discovery of these important protein structures to be made; investigators who had attacked the problem in nearly the same way but without use of the theory of resonance had been unsuccessful (Huggins 1943; Bragg, Kendrew & Perutz 1950).

The significance of the theory may be indicated by quoting the first two sentences of chapter 1 and the first sentence of the preface of the book on the theory of resonance by the late Professor George Willard Wheland (1944): 'Ever since the middle of the nineteenth century, the progress of chemistry, and especially of organic chemistry, has been closely associated with the development of the structural theory. One can, in fact, hardly question that this theory, more than any other single factor, must be given the credit for the remarkable advances that have occurred in the science during the last hundred years... The theory of resonance is the most important addition to chemical structural theory that has been made since the concept of the shared-electron bond was introduced by G. N. Lewis.'

It might well be thought that now, a half-century after the development of the theory, there would be no need to defend it from attack or misrepresentation.

During the first two decades after its formulation it was rather strongly attacked, usually because of the failure of critics to understand it. In the third edition of my book *The nature of the chemical bond* (1960), I clarified some of the points that had been raised. For example, it was suggested that the theory be abandoned because the individual valence-bond structures (such as the two Kekulé structures for benzene) that contribute to the normal state of a molecule are idealizations, and do not have independent existence. I pointed out that the theory of resonance is, in fact, no more artificial than the classical structure theory of organic chemistry, and that the contributing valence-bond structures in the theory of resonance are not more ideal (imaginary) than the structural elements of classical theory, such as the double bond. No other serious criticism or misrepresentation of the theory had come to my attention in recent years until I saw volume 22 of *Biographical memoirs of fellows of the Royal Society* (1976).

The memoir of Sir Robert Robinson in this volume (pages 415–527) was prepared by Lord Todd, P.R.S., and J. W. Cornforth, F.R.S., with the help of others, including M. J. S. Dewar for theoretical chemistry. Robinson, in addition to his great work in synthetic organic chemistry, had made important contributions to organic structure theory, anticipating in several ways the corresponding aspects of the theory of resonance in its application to organic compounds. I had mentioned his contributions, as well as those of Thiele, Arndt, Lowry, Lucas, and Ingold, in the first edition of my book (1939), as well as in later editions. His ideas and those of Ingold (whom I had met in 1930) had impressed me and had had some influence on my own work in the period from 1930 to 1933. I first met Robinson during World War II and became well acquainted with him in 1948, while I was Eastman Professor at Oxford. We got along well with one another. We talked about chemistry to some extent, and so far as I could tell we were in agreement about everything.

In the biographical memoir about Robinson there are several statements about me and about my work that are completely wrong, and others that are seriously misleading. The prestige and the generally reliable and authoritative nature of *Biographical memoirs* are such that wrong or misleading statements in these volumes should not remain uncorrected. I wrote to the authors, suggesting that they should publish a correction. One of them (Lord Todd) in reply suggested that it is my duty to prepare and to publish this defence of the theory of resonance against the criticisms that have been made of it.

2. The quantum-mechanical basis of the theory of resonance

The authors of the memoir (p. 466) discuss a disaffection that, they say, developed between Robinson and Sir Christopher Ingold. They then continue as follows: 'This disparity was accentuated by the introduction of the resonance theory by Pauling. This was claimed to be a direct consequence of wave mechanics

and hence to give a correspondingly valid description of chemical phenomena. Since the new quantum theory was at that time the latest and most exciting development in the whole of physical science, and since Pauling publicized his theory very skilfully, it quickly gained almost universal acceptance. The earlier classical electronic approach seemed entirely superseded by this new development and indeed Ingold at once adopted it. Robinson never accepted resonance theory and in this his instinct was, as usual, right. The arguments on which Pauling had based resonance theory later proved to be unsound, so the theory was at root, like Robinson's, purely phenomenological.'

The foregoing statements are quite wrong. The theory of resonance was not only 'claimed to be' a direct consequence of quantum mechanics, it *was* a direct consequence of quantum mechanics. The basic principle, as stated above, is that of the superposability of structures: the wave function for the normal state of a system can be represented as the sum (with the proper coefficients, such as to minimize the energy) of functions constituting any complete set. If we consider a system composed of two protons a considerable distance apart and a single electron, it is reasonable to describe its normal state as that of one normal hydrogen atom and one bare proton. There are, however, two such structures, and the quantum-mechanical principle, together with the equivalence of the two structures, requires that the correct wave function for the normal state of the system be more closely approximated by the sum of the two functions than by either one alone; that is, that there be resonance between the two structures. In the same way, as was pointed out by Slater (1931a), the equivalence of the two Kekulé structures of benzene requires that there be equal resonance between them; that is, that these two valence-bond structures contribute equally to the normal state of the molecule. The quantum-mechanical principles were similarly applied in a straightforward manner by both Slater (1931a) and me (1928, 1932a, c) to the question of the ionic or covalent character of bonds between unlike atoms. We both reached the conclusion that in general these bonds have a structure that corresponds to the superposition of the two structures (such as H^+Cl^- and H—Cl for hydrogen chloride). Slater (1931a) expressed the argument in the following way: 'Very general principles of wave mechanics tell us the outline of the treatment in these cases. The two explanations constitute two unperturbed states, from which the true one is to be found by linear combination, so that the real situation is intermediate between the two. If the energies of the two models are approximately the same, the real state will lie roughly half way between, while if one has a much lower energy than the other, that one will fairly accurately represent the situation. Moreover, if the two are combined, there will be a resonance effect in the energy, which will generally bring the real energy lower than that computed from either model separately.'

Over the years I have striven to develop a system of equations and rules that would permit the reasonably reliable prediction of some of the properties of any molecule or crystal. This system is largely empirical, although it has been in part

suggested by quantum-mechanical principles, including the theory of resonance. The semi-empirical nature of this system does not invalidate in any way the firm quantum-mechanical basis of the theory of resonance.

3. ERRORS AND MISCONCEPTIONS

The authors of the memoir state (p. 466) that Robinson's theory and resonance theory, when applied to the classes of organic compounds in which Robinson was interested, are 'effectively equivalent, leading to similar conclusions in all cases. The only difference lies in the formalisms used and that of resonance theory proved very misleading to organic chemists, giving rise to numerous errors and misconceptions.'

Some of the basic principles of quantum mechanics are so different from those of classical mechanics as to have made it hard for even physicists to understand and accept them, and it is not surprising, although it was unfortunate, that some organic chemists, with a poorer theoretical background, should have developed errors and misconceptions about the theory of resonance. An example is the confusion of resonance with tautomerism, mentioned in the memoir (p. 478) as having engendered numerous errors in the literature. This question was carefully analysed in my book, beginning with the first edition (1939). It is easy to distinguish between the two, except for the rare transition cases when the resonance frequency is approximately equal to the frequency of vibration of the nuclei. A modest amount of study of the theory of resonance should have been enough to prevent errors of this sort from being made.

4. UNEXCITED AND EXCITED STRUCTURES

In the memoir (p. 477) there is the statment that 'Pauling developed resonance theory as an intuitive generalization of the valence-bond method, in which the wave function for a molecule is written as a linear combination of so-called bond eigenfunctions. The latter in turn can be represented by formulae obeying the rules of valence but not of stereochemistry; the "bonds" may therefore correspond to real bonds in the molecule, or fictitious ones linking atoms that are too far apart to be bonded. The various structures are classed as unexcited, singly excited, doubly excited, etc., according to the number of such fictitious bonds. It can be shown that the contribution of a given structure to the ground state of a molecule is greater, the fewer fictitious bonds it contains; the unexcited (classical) structures make the greatest contributions. This seems to support a first order treatment in which only such structures are considered. As we have seen, such a treatment is homomorphous with the earlier electronic theory. This apparent justification later turned out to be fictitious, however. Although any single unexcited structure makes a greater contribution to the ground state of a molecule than does any single excited one, the number of excited structures is much greater.

In molecules even of moderate size, the vast number of excited structures allows them to swamp the unexcited ones; there is therefore no justification at all for neglecting the former (Pullman 1946).'

It is hard for me to understand how the authors could have been led to make these statements about the resonance theory. Slater (1931 b) had formulated his wave function to represent any valence-bond structure of a molecule. The function has the appropriate properties: it corresponds to strong attraction between atoms connected by a valence bond and to repulsion between other pairs of atoms. To refer to it as a 'so-called bond eigenfunction', as the authors do in the above quotation, rather than a 'valence-bond-structure eigenfunction', is unjust to John Slater. I devised the graphical method of easily calculating the coefficients of the various integrals (1933), and Wheland and I introduced the names unexcited, singly excited, etc. (1933). We gave the name 'formal bonds' to the lines in the excited structures connecting atoms not adjacent to one another (not 'fictitious bonds', which may be misleading). These formal bonds are needed to define the wave functions of a complete set; they connect electrons with opposite spin in a carefully defined way.

The statement quoted above suggests that neglect of the excited structures and consideration only of the unexcited structures is an essential part of the theory of resonance, and that it has been shown to be unjustified. The fact is that my colleagues and I gave thorough consideration to the effects of the excited structures. Sherman and I (1933) showed that the characteristic properties of various unsaturated hydrocarbons can be accounted for by consideration of the excited as well as the unexcited valence-bond structures for the molecules. Wheland and I (1933) studied the condensed aromatic hydrocarbons. Naphthalene has 42 valence-bond structures in its canonical set. The 3 unexcited structures alone were found to contribute 68 % of the total resonance energy, the 16 singly excited structures an additional 30 %, and the 19 doubly excited plus the 4 triply excited structures only 2 %. For some properties, consideration of the unexcited structures alone gives results in rather good agreement with experiment; an example is the carbon–carbon bond lengths. For other properties excited structures must also be taken into consideration. The discussion of this aspect of the theory of resonance in the memoir is based upon an incorrect assumption about the theory; it is equivalent to setting up a straw man and then shooting him down.

Lord Todd has kindly called my attention to a paper by Dewar & Longuet-Higgins (1952) entitled 'The correspondence between the resonance and molecular orbital theories'. In this paper it is stated (incorrectly) that in the theory of resonance it is assumed that 'the wave function of a molecule can be represented sufficiently well as a linear combination of wave functions for the unexcited canonical forms or classical structures. This implies that if there is only one classical structure, the wave function corresponding to this structure should represent the molecule adequately.'

In fact, however, such as assumption is not a part of the theory of resonance.

Reference to the early papers on resonance or to my book (1939) or Wheland's book (1944) provides many examples of discussions of resonance involving excited structures and ionic structures.

Dewar & Longuet-Higgins wrote that this assumption and two other assumptions that they ascribe to the theory of resonance have very little basis in theory. They then carried out a rather general molecular-orbital treatment of hydrocarbon molecules, and concluded that 'It is here shown that a remarkable correspondence exists between the resonance theory and the molecular orbital method; and it is suggested that the resonance theory owes its success more to this correspondence than to the validity of its own premises.' Their work contributed an additional plank to the theoretical foundations of the theory of resonance, but their statement that its premises had previously lacked a sound basis in theory is invalid, because they had formulated assumptions about the theory of resonance that were not in fact a part of the theory. The same error was repeated in the memoir, as quoted above.

5. CHEMICAL REACTIVITY

The discussion of chemical reactivity in the memoir (pages 477 and 478) read as follows: 'The special chemical behaviour of a conjugated molecule depends on the possibility of electromeric rearrangement during reactions rather than on any inherent peculiarity of the molecule itself. Indeed, one of the major pitfalls of resonance theory was the tendency to try to explain the reactions of molecules in terms of their structure. Robinson believed, correctly, that reactivity depends on the electronic reorganization which takes place during a reaction and which he represented in terms of electromeric shifts. There is no reason why the electrons in the reactants should show any preliminary polarization in this sense. In current terminology, we would say that reactivity depends on the energies both of the reactants and of the transition state, not on any properties of the reactants alone. Because of Pauling's unfortunate contribution, this basic truth was largely overlooked for a generation.'

I find it very hard to understand why this statement, which is completely false and unsubstantiated, should have been made about me. I was in the California Institute of Technology in the 1920s, when R. C. Tolman, O. K. Rice, L. S. Kassel, and H. C. Ramsperger were making important contributions to the theory of the rate of chemical reactions, and I became quite familiar with the theory. My first published discussion of resonance theory in relation to reaction rate dealt with the Mills–Nixon effect, a change in directed orientation of substituents in a hydroxy-substituted benzene ring by other substituents, such as trimethylene in 5-hydroxyhydrindene, that change the values of the bond angles (Sutton & Pauling 1935). Sutton and I pointed out that the 5-membered hydrindene ring would stabilize the Kekulé structure with a single bond in the 1, 2 position (common to the two rings) relative to the other Kekulé structure, and hence would cause the double-bond character in the 5,6 position to be greater than that in the 4,5 position.

The known property of hydroxyl to direct substituents preferentially to the adjacent position connected by a double bond would thus cause the 6 position to be favoured over the 4 position. A valence-bond calculation was made of the changed amounts of double-bond character, and then, with some reasonable assumptions, a calculation was made of the ratio of the activation energies for substitution in the two positions. In the same year Wheland and I (1935) published a paper on a quantum-mechanical discussion of orientation of substituents in aromatic molecules. We discussed substitution in several monosubstituted benzenes, C_6H_5R, in pyridine, C_5H_5N, and in naphthalene, $C_{10}H_8$, using arguments rather similar to those used by Robinson, but supported by quantum-mechanical calculations (with use of the molecular-orbital method). We did not assume that the reaction rates were determined by the electron distribution in the reactant aromatic molecule. Instead, we calculated the contribution of this molecule to the structure of the activated complex, as described in the following words: 'In the molecule C_6H_5R, with R attached to carbon atom 1, the electron distribution may be such as to place an excess or a deficiency of electrons on the various carbon atoms 2 to 6. Moreover, the electron distribution may be changed somewhat on the approach of a group R' to one of the carbon atoms ("polarization" of the molecule by the group). We assume *that the rate of substitution of R' for hydrogen on the ith carbon atom increases with increase in the negative charge of the ith carbon atom when the group R' approaches it*. We thus take into consideration, in addition to the permanent charge distribution, the changes in it caused by the approaching group. There are two principal ways in which the charge distribution is affected by the substituent R. The first, called the *inductive effect*, results when the electron affinity of this group is appreciably larger, or smaller, than that of the hydrogen atom which it replaces... The second way in which the substituent R affects the charge distribution of the molecule is called the *resonance effect* (or sometimes the *tautomeric* or *electromeric* effect). This results when the molecule resonates among several electronic structures... These ideas have arisen through the combined efforts of a large number of different workers, among whom may be mentioned Fry, Stieglitz, Lapworth, Lewis, Lucas, Lowry, Robinson, and especially Ingold.'

Closely similar discussions are given in my book and the book by Wheland. It is clear that our attack on the problem of chemical reactivity was essentially the same as that of Robinson, except for our quantum-mechanical refinement of it. I can find no basis whatever in these papers or my other publications for what the authors of the biographical memoir of Robinson call 'Pauling's unfortunate contribution'.

6. CONCLUSION

The theory of resonance is an important and useful part of the modern structure theory of both inorganic and organic chemistry. It owes its origin to and has a firm basis in the principles of quantum mechanics. In some of its applications it resembles the electronic theory of organic compounds that was developed by Sir Robert Robinson in the period around 1926.

Some incorrect and seriously misleading remarks about the theory and about my participation in its development are contained in the biographical memoir of Robinson (Todd & Cornforth 1976). It is pointed out in the foregoing pages that these remarks are not based on facts but are based entirely on misunderstanding or incompleteness of knowledge of the nature and early history of the theory of resonance.

REFERENCES

Bragg, W. L., Kendrew, J. C. & Perutz, M. F. 1950 *Proc. R. Soc. Lond.* A **203**, 321.
Dewar, M. J. S. & Longuet-Higgins, H. C. 1952 *Proc. R. Soc. Lond.* A **214**, 482.
Heisenberg, W. 1926 *Z. Phys.* **39**, 499.
Heitler, W. & London, F. 1927 *Z. Phys.* **44**, 455.
Hückel, E. 1931 *Z. Phys.* **70**, 204.
Huggins, M. L. 1943 *Chem. Rev.* **32**, 195.
Pauling, L. 1928 *a Chem. Rev.* **5**, 173.
Pauling, L. 1928 *b Proc. nat. Acad. Sci. U.S.A.* **14**, 359.
Pauling, L. 1929 *J. Am. chem. Soc.* **51**, 1010.
Pauling, L. 1931 *a J. Am. chem. Soc.* **53**, 1367.
Pauling, L. 1931 *b J. Am. chem. Soc.* **53**, 3225.
Pauling, L. 1932 *a J. Am. chem. Soc.* **54**, 988.
Pauling, L. 1932 *b Proc. nat. Acad. Sci. U.S.A.* **18**, 293.
Pauling, L. 1932 *c J. Am. chem. Soc.* **54**, 3570.
Pauling, L. 1933 *J. chem. Phys.* **1**, 280.
Pauling, L. 1939 *The nature of the chemical bond.* Ithaca, N.Y.: Cornell University Press. 2nd ed. 1940, 3rd ed. 1960.
Pauling, L. & Corey, R. B. 1950 *J. Am. Chem. Soc.* **72**, 5349.
Pauling, L. & Corey, R. B. 1951 *Proc. nat. Acad. Sci. U.S.A.* **37**, 729.
Pauling, L. & Sherman, J. 1933 *J. chem. Phys.* **1**, 679.
Pauling, L. & Wheland, G. W. 1933 *J. chem. Phys.* **1**, 362.
Pauling, L. & Wilson, E. B. Jr 1935 *Introduction to quantum mechanics.* New York: McGraw-Hill Book Co.
Slater, J. C. 1931 *a Phys. Rev.* **37**, 481.
Slater, J. C. 1931 *b Phys. Rev.* **38**, 1109.
Sutton, L. E. & Pauling, L. 1935 *Trans. Faraday Soc.* **31**, 939.
Todd, Lord & Cornforth, J. W. 1976 *Biogr. Mem. Fellows R. Soc. Lond.* **22**, 415–527.
Wheland, G. W. 1944 *The theory of resonance and its application to organic chemistry.* New York: John Wiley and Sons.
Wheland, G. W. & Pauling, L. 1935 *J. Am. chem. Soc.* **57**, 2086.